Steel Industry Slags Compared with Calcium Carbonate in Neutralizing Acid Mine Soil[1]

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ABSTRACT. Ohio has substantial lands impacted by surface mining for coal and an active steel industry. Steel industry slags have been used as liming compounds for agriculture and acid mine soil reclamation. This 3-year study evaluates slags from Ohio steel mills in greenhouse trials where these materials are compared to reagent grade $CaCO_3$ in their ability to improve plant growth on acid mine soil. The objectives of this study were to evaluate the effectiveness of these materials at two rates of application in raising acid mine soil pH and to address concerns about metals in such slags. Three slags and reagent grade $CaCO_3$ were applied at rates equivalent to 12.5 and 25 g $CaCO_3$ kg^{-1} soil on acid mine soil (pH = 3.5). Five consecutive crops of oats (*Avena sativa* L.), wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), wheat and soybean (*Glycine max* (L.) Merr.) were grown and harvested at the seedling stage. The slags and $CaCO_3$ increased yields (P <0.01 level) compared to unlimed control pots. Soil and plant Ca were increased and plant Al and Mn decreased by application of all four materials. The slags increased soil and plant Mg. Particle size of the slags was somewhat coarse which decreased their effectiveness, but overall these slags proved to be satisfactory liming materials. The fineness efficiency developed for carbonate forms of lime may not adequately characterize slag effectiveness. Micronutrient metals including iron were not found to be in excess in plant tissue treated with slags despite the steel slags' high Fe content.

OHIO J SCI 105 (4):79–87, 2005

INTRODUCTION

Ohio has thousands of hectares of lands disturbed by resource extraction, principally the surface mining of coal, sand and gravel, limestone, and other building stone. Sutton and Dick (1987) reported in a review of reclamation of lands disturbed by mining that Ohio had 138,000 ha of surface mined lands of which 111,000 ha (80%) were coal mine sites located in the southeast region of the state's Appalachian Plateau. Many of these coal mine sites contain FeS_2 (mascarite and pryrite) that can become sources of extreme soil acidity and acid mine drainage. Acid conditions solubilize metals and increase concentration of Al, Mn, and Fe to toxic levels, severely restricting plant growth and leading to increased soil erosion sources of sediments and acid mine drainage. In their review paper, Pichtel and others (1994) discussed reclamation strategies that made use of some of society's by-products, such as sewage sludge (biosolids), papermill sludge, and power plant fly ash, in attempting to create a soil environment that would support vegetative cover, such as trees and forage plants, on acid mine soil. They reported more success with biosolids and papermill sludge than with power plant fly ash on extremely acid mine soil sites. Another such industrial by-product is steel industry slag. Ohio, like other Midwest and Northeast states, has significant steel making capacity. Iron and steel slag sales in the United States during 1996, 1997, and 1998 indicate that over half of all sales are generated in the North Central States of Illinois, Indiana, Michigan, and Ohio (Kalyoncu and Kaiser 1998; Kalyoncu 1999).

Slags are nonmetallic byproducts of iron and steel making, and they are unique to the limestone sources used and the specialty steel being manufactured. They are comprised of Ca and Mg silicates and are able to supply Ca and/or Mg and also neutralize acidity. Typically a blast furnace with an ore feed with 60 to 66% iron would generate 220 to 370 kg of slag for each metric ton of pig iron produced, and steel slag outputs are typically 20% weight/weight (w/w) of steel output (Kalyoncu and Kaiser 1998). While blast furnace and steel furnace slags have many uses, one historic and widespread use has been as a liming material.

The use of steel industry slags as a substitute for traditional limestone has a substantial history in Ohio (Williams 1946; Volk and others 1952; Jones 1968). Volk and others (1952) evaluated granulated slag (water quenched), air-cooled slag, and dolomitic limestone reconstituted by combinations of various sieve sizes into "ag screenings," "ag meal," and "ag ground" size grades as defined by Ohio's limestone law. They compared the three materials in both greenhouse and field studies at Wooster, Canfield, and St. Clairsville, OH. The granulated and air-cooled slags were much higher in SiO_2 and Al_2O_3, somewhat higher in Ca, and much lower in Mg than the dolomitic limestone at all 3 field study locations. Greenhouse pot tests for the correction of soil acidity were conducted with Wooster silt loam (Fine-loamy, mixed, mesic Oxyaqic Fragiudalfs) and plant growth performance in the greenhouse at several levels of each liming material were performed with Trumbull silty clay loam (Fine, illitic, mesic Typic Epiaqualfs). In field studies the average hay yields were higher for granulated slag than for air-cooled slag or limestone at each size gradation (screenings, meal, and ag ground). Air-cooled slag and dolomitic limestone were equally effective when they had the same particle size distribution. In greenhouse studies granulated slag

[1]Manuscript received 7 February 2004 and in revised form 22 June 2005 (#04-05).

and dolomitic limestone were more effective at correcting soil acidity than air-cooled slag. Since air-cooled slags produced crop yields quite comparable to limestone and yet did not raise pH as effectively, the studies indicated that crop yield response to the slags involved more than simply neutralizing soil acidity.

Jones (1968) reevaluated the effectiveness of granulated steel industry slag in field studies on acid Canfield silt loam (Fine-loamy, mixed, mesic active Aquic Fragiudalfs) of pH 5.5. He compared the performance of slag to comparable rates of calcitic and dolomitic limestone and concluded that granulated slag was as effective at the two rates used (3.36 and 6.72 Mg ha^{-1}) as either type of limestone. Crop yields were equal or slightly higher for the slag treatment compared to the calcitic and dolomitic lime treatments. When soil and plant Ca and Mg were measured, the granulated slag and dolomitic limestone both boosted the soil and plant Mg to a significantly greater degree than did the calcitic limestone. This was because of the high Mg content of the granulated slag (12% MgO equivalent) and the dolomitic lime.

Rodriguez and others (1994) evaluated the performance of Basic Linz-Donowitz slag as a liming material for pastures in Northern Spain. In European steel manufacturing, approximately 150 kg of such slag are generated for every 1000 kg of steel produced. The slag used was 290 g kg^{-1} Ca and 50 g kg^{-1} Mg (w/w). In addition, it contained substantial quantities of Fe, Se, and Mn, and traces of Pb, Zn, Cu, K, Na, and Cd. The slag application resulted in a decrease in Al saturation and increases in Ca and Mg saturation of the soil cation exchange capacity. Slag applications resulted in higher Ca, Mg, and P concentrations and higher yields than the untreated plots. During the 3-year study, slag application reduced plant K and Mn concentrations.

Oguntoyinbo and others (1996) compared four liming materials: basic slag, cement flue dust, indigenous limestone, and imported slaked lime $Ca(OH)_2$ on two acid soils in greenhouse trials in Nigeria. The relative effectiveness at neutralizing soil acidity was $Ca(OH)_2$ > basic slag > cement flue dust > limestone. Lime requirements were related to soil exchangeable Al^{3+} on both soils. There were no significant differences in plant yield among lime sources.

The soils of the North Central/Northeast US need periodic treatment (every 3-6 yrs) with liming materials to correct soil acidity, enhance nutrient availability and microbial activity, and to restore the supplies of exchangeable Ca and Mg (McLean and Brown 1984). Ohio monitoring networks for acid precipitation show rain and snow to have a pH of 4.0 to 4.4, lower than the normal pH 5.6 of water in equilibrium with ambient atmosphere CO_2 (National Atmospheric Deposition Program, National Trends Network, 1988, 1989; data for Wooster, OH).

The objectives of this study were to evaluate the effectiveness of these slag materials with the size characteristics provided at raising soil pH for acid mine soil remediation, and to note the uptake of metals when slags were used compared to $CaCO_3$.

METHODS AND MATERIALS

Three steel industry slags were supplied by Stein Inc., Broadview Heights, OH, from LTV steel in Cleveland, OH, or USS Kobe in Lorain, OH. These slags were identified as blast furnace slag (BFS), non-metallic steel slag (NMSS) poured off from slag far from the molten steel, and metallic steel slag (MSS) poured from the slag very close to the molten steel. Table 1 gives particle size and chemical properties of the slags and the reagent grade $CaCO_3$. The particle size data was obtained by sieving the slags. The chemical analyses were performed by The Ohio State University Research and Extension Analytical Laboratory (REAL), Wooster, OH, and the Penn State Ag Analytical Laboratory, University Park, PA, on samples digested in concentrated perchloric or nitric acid. Penn State's soil test lab procedures used Mehlich III for soil P and extractable cations (Wolf and Beegle 1995) and pH in water (1:1) and SMP buffer to assess the soil active and exchangeable acidity respectively (Eckert and Sims 1995). The change in supporting laboratories was made necessary by Ohio State's closure of the REAL Lab in December 1998.

The greenhouse studies used an acid mine soil from Ohio Agricultural Research and Development Center (OARDC) Unit 2 in Caldwell, OH. Hall (1977) proposed classification of the mine soils at this location as Barkcamp (Loamy-skeletal siliceous, acid, mesic Typic Udorthents) and Enoch (Loamy-skeletal, siliceous, acid, mesic Typic Udorthents) series based on pH and the potential for oxidation of FeS_2 minerals. The mine soil pH collected at Caldwell Unit 2 averaged pH 3.5. Air dried and ground mine soil at 1.5 kg per pot was amended with four materials: blast furnace slag (BFS), steel furnace slag (NMSS), metallic steel slag (MSS), and reagent grade $CaCO_3$ at two rates: 12.5 g kg^{-1} and 25 g kg^{-1} of 100% $CaCO_3$ equivalent material (equivalent to 16.7 and 33.3 Mg ha^{-1}, respectively). The experiment was designed as a 4 × 2 factorial (4 treatments at 2 rates). Each treatment was replicated four times and placed on the available greenhouse bench with treatments completely randomized on the bench space. The statistical analyses utilized the General Linear Model of SAS for analysis of variance and construction of appropriate orthogonal comparisons. The pots were watered with deionized water throughout the course of these experiments with the opportunity for free drainage at the bottom of the pots. On 30 April 1998, 20 seeds per pot of oat cultivar (cv) 'Armor' were planted 1.0 cm deep in each pot. After germination and emergence, all pots were treated three times with 100 ml of 0.01 M KH_2PO_4 and 0.01 M KNO_3. The plants were harvested by cutting at the soil surface on 3 June 1998, at about the 4-leaf stage (~20 cm tall), oven dried, weighed, and saved for tissue analysis. After the oat crop was harvested, all soils were crushed in the top 5.0 cm of each pot, a small (15-20 g) portion was removed for soil pH measurement, and the pots were reseeded with 20 seeds of wheat (cv 'Freedom') on 2 October 1998. The wheat seedlings (Feekes Stage 6) were harvested by cutting at the soil surface on 9 December 1998, oven dried, weighed, and saved for subsequent analysis. After the

TABLE 1

Chemical and physical characteristics of slags† and $CaCO_3$ used in these studies.

Identification	Non-Metallic Steel Slag NMSS	Metallic Steel Slag MSS	Blast Furnace Slag BFS	$CaCO_3$
pH	12.5	12.5	10.3	8.2
$CaCO_3$ Equiv (%)	79.8	65.0	81.1	100.0
ECCE	22	20	27	100
Ca (%)	22.2	26.2	25.2	40.0
Mg (%)	5.53	2.75	5.07	0.0
Al (%)	1.64	1.62	3.79	0.0
P (mg kg^{-1})	2286	980	59	0.0
Fe (%)	15.9	21.6	0.88	0.0
Mesh Size	(%)			
>8	5.1 ± 1.0	48.5 ± 2.7	36 ± 6.1	—
8-20	18 ± 2.1	23.0 ± 0.5	35 ± 5.0	—
20-60	18 ± 2.8	11.7 ± 0.7	23 ± 5.5	—
60-100	6.7 ± 0.3	4.9 ± 0.5	5.9 ± 2.6	—
<100	6.5 ± 2.0	11.9 ± 1.2	4.0 ± 1.6	100
Fineness eff. ††	28	31	33	100

† Mean and standard deviation of four replicate sieving analyses.
†† Fineness efficiency (>8 mesh × 0.0, 8-60 mesh × .40, <60 mesh × 1.0, Troeh & Thompson (1993).

wheat harvest, all the soil was crushed again and 40 g of commercial peat moss (equivalent to 53 Mg ha^{-1}) was mixed with the soil in each pot. Corn was planted on 1 February 1999 at the rate of 5 seeds of cv 'Pioneer 3525' per pot and thinned to 3 seedlings per pot two weeks after emergence. The corn seedlings (tallest plants ~40 cm) were harvested at the soil surface on 26 April 1999, oven dried at 70° C, and weighed. The soils were sampled for pH, and the soil in the surface of the pots crushed and replanted with 15 seeds per pot of wheat (cv 'Hopewell') on 4 October 1999. Plants (Feekes stage 6) were harvested at the soil surface on 29 November 1999, oven dried at 70° C, and weighed. The pots of soil media were stored outside in the rain and snow of winter 2000 then returned to the greenhouse and seeded with four seeds of soybean ([Roundup Ready] cv 'Dynagro 3280') on 7 April 2000. Pots were watered three times per week with deionized water and any pots with less than 4 seedlings per pot were replanted on 21 April 2000. Plants were thinned to 3 per pot on 1 May 2000, and the seedling plants (~25 cm tall with 3 or 4 trifoliate leaves) were harvested at the soil surface on 8 June 2000. The harvested soybean seedlings were oven dried at 70°C, weighed, and sent to Penn State's lab for mineral analyses. Soil samples were collected from the pots with a probe sampling the full depth of the pots and compositing together 3 or 4 cores from each pot.

RESULTS

Slag and Calcium Carbonate Product Characteristics

The three slag products all had very low effective $CaCO_3$ equivalent (ECCE) values, which are based on the particle sizes and calcium carbonate equivalent of each material (Table 1). Both steel furnace slags (NMSS and MSS) were higher in pH than BFS or $CaCO_3$. The order of particle size from coarse to fine was NMSS > MSS > BFS > Reagent grade $CaCO_3$. The order of $CaCO_3$ equivalence was $CaCO_3$ > BFS > NMSS > MSS. Since constant application rates of $CaCO_3$ equivalent were applied for all four materials, the material with the lowest effective calcium carbonate equivalence based on the particle size would be expected to be less effective at raising the pH of the acid mine soil. This was not the case (see Tables 2, 3). Munn (2003) noted similar disparities with slags in a field study with turfgrass in that slags, while not as effective as commercial dolomitic lime, were more effective than their size efficiency would have predicted at raising soil pH of acid silt loam topsoil. The two steel slags (NMSS and MSS) were

TABLE 2

Soil test results – samples collected November 1998 and April 1999.

Neutralizing Source (NS)	Nov 1998 Soil pH	Soil P mg kg^{-1}	Acidity	K	Mg	Ca	CEC †	April 1999 Soil pH
			cmoles$_c$ kg^{-1}					
Control Unlimed	3.5	8.0	21.2	0.20	0.75	1.2	17.2	3.6
BFS (12.5 g kg^{-1})	4.9	4.5	3.4	0.16	3.58	12.3	19.3	6.8
BFS (25 g kg^{-1})	5.3	2.5	2.6	0.13	3.90	14.5	20.4	7.3
NMSS (12.5 g kg^{-1})	6.2	5.5	2.0	0.11	3.93	26.4	21.1	7.3
NMSS (25 g kg^{-1})	7.1	13	0.0	0.11	5.53	40.7	20.6	7.6
MSS (12.5 g kg^{-1})	6.0	4.5	2.0	0.12	2.38	19.2	19.5	7.2
MSS (25 g kg^{-1})	6.8	10	1.0	0.11	3.18	35.7	19.3	7.5
$CaCO_3$ (12.5 g kg^{-1})	6.9	4.5	0.0	0.13	0.73	29.1	15.9	7.3
$CaCO_3$ (25 g kg^{-1})	7.2	3.0	0.0	0.13	0.75	33.5	15.9	7.3
LSD (0.05)	0.3	3.5	4.50	0.03	0.51	4.9	1.1	0.3

—— ANOVA Probability (f) ——

Source	df	Nov 1998 Soil pH	Soil P	Acidity	K	Mg	Ca	CEC †	April 1999 Soil pH
Neutralizing Source	4	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Rate	1	0.0001	0.0128	0.0001	0.147	0.0001	0.0001	0.688	0.0001
NS × Rate	3	0.009	0.0009	0.0030	0.489	0.0008	0.0003	0.180	0.0539

† CEC calculated by summing extractable Ca, Mg, K, and acidity.

also higher in metals common to steel alloys such as Cr, V, and Co. The BFS by contrast was higher in the metals Ba, Sr and Be (data not shown).

Effects of Slags and Calcium Carbonate on Acid Mine Soil and Plant Growth

The acid mine soil was an extremely toxic environment for plants. The dry matter yields of all crops are presented in Table 4. The ANOVA for treatments, rate, and interaction on yield showed significant differences at the (P <0.01) level (Table 4). For the first crop in the non-treated control plots, the oat germination was low and seedlings quickly died from the low soil pH and associated Al toxicity. The three slags (BFS, NMSS, MSS) and reagent grade $CaCO_3$ all resulted in successful germination and seedling growth of oat plants. Although the higher rate of application did not always result in the optimum growth of oat seedlings, in general the slags were nearly as effective as the $CaCO_3$ at remediating the extreme acidity of the acid mine soil and improving plant growth. The differences between neutralizing sources were not significant at the P <0.05 level (Table 5). This was the case despite the much lower overall effective $CaCO_3$ equivalence of slags because of their coarser particle size (Table 1). The control treatment plants did not survive in the first two crops (oats and wheat) produced. Therefore only results of the tissue analysis of the four surviving treatments may be compared with each other. Wheat plant yields were significantly affected by neutralizing material source at the P <0.01 level. The yields were in the sequence $CaCO_3$ > NMSS > MSS >BFS (Table 4.) Control plants died early and provided only a bit of dried residue at seedling stage harvest.

After the first two crops, the soil had been crushed and amended with peat moss. This organic matter addition is part of common reclamation practice (Sutton and Dick 1987), and it enhanced growth of all plants, especially for the unlimed control pot plants. The third crop in the sequence was corn, and corn plant dry matter yields were not significantly different (P <0.05) for neutralizing source, rate, or interaction (Table 5). The 4th crop was another wheat crop. The neutralizing source was a significant (P <0.05) cause of differences in plant dry matter yields with the order of yields being BFS > MSS > NMSS > $CaCO_3$ > Control. In the 5th crop grown, soybeans, the effects of neutralizing source, rate, and rate by source interaction were all significant at the P <0.05 level. The highest yield came with MSS and then BFS. In three of the four neutralizing materials,

TABLE 3

Soil test results – samples collected 9 June 2000.

Neutralizing Source (NS)		Soil pH	Soil P mg kg^{-1}	Acidity	K	Mg	Ca	CEC
				cmoles$_c$ kg^{-1}				
Control Unlimed		4.8	34.0	4.90	0.4	0.6	1.9	7.8
BFS (12.5 g kg^{-1})		5.5	24.3	2.13	0.2	2.1	8.7	13.0
BFS (25 g kg^{-1})		7.0	22.9	0.00	0.2	3.4	13.8	17.4
NMSS (12.5 g kg^{-1})		7.2	29.3	0.00	0.1	2.4	16.2	17.5
NMSS (25 g kg^{-1})		7.7	37.8	0.00	0.1	3.5	28.8	18.6
MSS (12.5 g kg^{-1})		6.7	27.0	1.5	0.1	1.7	13.7	16.9
MSS (25 g kg^{-1})		7.5	32.3	0.0	3.6	2.1	22.9	17.2
$CaCO_3$ (12.5 g kg^{-1})		6.9	25.4	1.0	0.1	0.5	14.3	15.0
$CaCO_3$ (25 g kg^{-1})		7.5	24.5	0.0	0.1	0.5	27.1	15.6
LSD 0.05		0.4	9.2	5.86	3.36	.026	3.0	1.2
				ANOVA Probability (f)				
Source	df							
Neutralizing Source	4	0.001	0.014	0.0001	0.521	0.0001	0.0001	0.0001
Rate	1	0.001	0.227	0.0001	0.296	0.0001	0.0001	0.0001
NS × Rate	3	0.005	0.377	0.0028	0.366	0.0001	0.003	0.0001

the higher soybean seedling plant yield came at the lower of the two rates of application, 12.5 g of $CaCO_3$ kg^{-1} versus 25 g of $CaCO_3$ kg^{-1} of soil (Table 4).

The plant growth in the soil prior to crushing and amendment with peat moss included two crops, oats and wheat. The following generalizations have been made from the data in Table 5. These plant tissue results represent the crops grown before soils were crushed and amended with peat moss. The plant P varied with amendment and level of lime treatment application (data for 12.5 g kg^{-1} not shown) with higher plant P at the higher rate of lime treatment, the plant K levels were higher than the sufficient level for all four amendments at both levels of application. The plant Ca and Mg responded to rate of neutralizing material applied (that is, higher in the higher rate of application). Order of oat plant Ca content was $CaCO_3$ > MSS > NMSS > BFS. The BFS treatment had the highest oat plant Mg content. The plant Mg content of NMSS, MSS, and $CaCO_3$ were similar and in the low end of the sufficient range. Plant tissue micronutrients appeared to be similar in plant tissue from pots amended with any of the four materials with the exception of the BFS treatment, which was higher than the sufficient range for Mn and higher than the plant Mn in any of the other treatments. The Fe content in the steel slags was quite high, but the crops grown on acid mine soil amended with these steel slags were not abnormally high in plant tissue Fe. All four amendments were able to raise soil pH to 7.0 or higher at the 25 g $CaCO_3$ kg^{-1} soil rate applied (Table 2). This rate (25 g kg^{-1}) represents the case where metal-loading rates from the slags might be expected to be too high, if that problem should occur with any of the materials studied. Higher rates of $CaCO_3$ equivalent applied resulted in the higher soil pH for each liming material (Tables 2 and 3). The BFS soil pH declined in the final months of the study to 5.5 (Table 3), the pH level below which Al toxicity is very much increased (McLean and Brown, 1984). BFS had a higher effective calcium carbonate rating than NMSS or MSS, but was less effective at the 12.5 g kg^{-1} rate at neutralizing acidity than the other two slags.

Corn and soybean and wheat crops were grown after the pots were amended with peat moss. Wheat tissue was not analyzed for this second wheat crop. The results for corn plant tissue mineral composition are presented in Table 6 for the 25 g kg^{-1} rate of acid neutralizing materials. Only a composite tissue sample could be assembled for analysis in the control pots. This composite sample was abnormally high in N and P. These nutrients may have been concentrated by very limited dry matter growth. The levels of Mn, Fe, Zn, and Al in the corn plants from the control pots were high since these pots averaged a soil pH of 3.7 when soil

TABLE 4

Crop dry matter yields for acid mine soil amended with slags and $CaCO_3$.

Neutralizing Source (NS)	Rate ($g\ kg^{-1}$)	Oats	Wheat 1998	Corn (g/pot)	Wheat 1999	Soybeans
Control	0.0	0.0	0.03	0.21	1.37	0.56
BFS	12.5	2.10	1.79	11.72	3.20	2.67
	25.0	1.73	1.13	9.89	3.16	1.73
NMSS	12.5	2.06	1.64	10.66	2.59	1.84
	25.0	2.57	1.58	9.92	2.74	2.11
MSS	12.5	2.02	1.45	9.80	2.81	2.28
	25.0	2.42	1.70	9.20	3.15	1.35
$CaCO_3$	12.5	2.02	1.96	9.53	2.38	1.79
	25.0	2.19	2.52	8.12	2.77	1.66
LSD 0.05		0.44	0.56	2.46	0.58	0.60
ANOVA Probability (f)						
Sources	df					
Neutralizing Source	4	0.311	0.001	0.163	0.001	0.001
Rate	1	0.256	0.068	0.085	0.068	0.007
NS × Rate	3	0.205	0.872	0.891	0.873	0.014

samples were collected and analyzed after the corn plants were harvested. The treatments of slag or pure $CaCO_3$ all had low plant tissue P and the reagent grade $CaCO_3$ treatments had low plant tissue Mg. No metals such as Fe, Mn, or Zn were abnormally high in these plant tissue samples.

The soybean plant seedling elemental composition is reported in Table 6 for the 25 $g\ kg^{-1}$ rate of acid neutralizing materials. Most of the slag and lime treatments were low in plant P and K. Control plants were higher in P and K, possibly because of low dry matter production, which concentrated these nutrients. Plant Ca was high in all plants except the untreated controls. Mg was high in all plants except the plants of the untreated controls and those receiving only reagent grade $CaCO_3$. The soybean plant Al, Mn, Zn, and Fe levels all declined with the higher soil pH associated with the slag and lime treatments, particularly the 25 $g\ kg^{-1}$ rate of application. Again no metals such as Fe, Mn, or Zn seemed abnormally high in these plant tissue samples even at the 25 $g\ kg^{-1}$ rate. The corn and soybean plants were larger at harvest than the small grains and no interpretive database was available for a "normal or sufficient" range of nutrient metals in these crops at this growth stage.

Soil Test Results

Soil tests results before the addition of peat are shown in Table 2 (1998) and after amendment with peat in Table 2 (1999) and Table 3 (2000). Soil extractable (available) P was increased by some treatments and decreased by others. The soil K levels were decreased by all four neutralizing material treatments compared to the control pots. This may represent enhanced plant growth and K uptake from the pots or displacement of K from the CEC sites of the soil by the Ca and Mg from the added lime and slag allowing K to leach. These pots did have the opportunity for leaching and were watered over the course of all the crops with deionized water. Soil exchangeable Ca levels were increased by all four treatments. The soil exchangeable Mg level was increased by BFS, SFS, and MSS but, as would be expected, not by the reagent grade $CaCO_3$. Soil exchangeable acidity was

TABLE 5

Wheat and oat seedling plant tissue mineral composition at 25 g kg^{-1} rate.

Treatment	P	K	Ca	Mg	Mn	Fe	Zn	Al
	(%)				(mg kg^{-1})			
Corn								
Control Unlimed	—	—	—	—	—	—	—	—
BFS (25 g kg^{-1})	0.168	3.51	0.375	0.254	290	32	30	33
NMSS (25 g kg^{-1})	0.235	3.82	0.442	0.211	171	44	20	28
MSS (25 g kg^{-1})	0.242	3.81	0.472	0.196	184	42	22	23
$CaCO_3$ (25 g kg^{-1})	0.259	3.92	0.517	0.206	87	44	24	19
LSD (0.05)	0.05	0.37	0.05	0.015	21	8	3	12
Wheat								
Control Unlimed	0.51	2.13	0.39	0.56	503	246	222	1439
BFS (25 g kg^{-1})	0.23	2.49	0.48	0.33	688	57	14	38
NMSS (25 g kg^{-1})	0.20	2.30	0.65	0.29	494	41	10	22
MSS (25 g kg^{-1})	0.21	2.22	0.66	0.25	539	35	10	16
$CaCO_3$ (25 g kg^{-1})	0.20	2.70	0.59	0.17	57	39	11	19
LSD (0.05)	0.10	0.56	0.15	0.04	106	111	44	591
Sufficient Range †	0.21-	1.51-	0.21-	0.15-	16-	11-	21-	—
	0.50	3.00	1.00	0.60	200	300	70	—

† Agronomy Extension Staff (1995).

decreased by all four treatments and inversely related to the noted increase in soil pH, but BFS was less effective than NMSS, MSS, or reagent grade $CaCO_3$. Based on its effective calcium carbonate equivalence, BFS should have outperformed the other two slag products. The particle size effectiveness rating developed for limestone may not be accurate for silicate slags.

DISCUSSION

Volk and others (1952) performed their field trials and greenhouse studies with two slags (granulated and air-cooled) and dolomitic limestone that was separated by sieving and then reconstituted to create three size grades of each material: screenings, meal, and ground. These size grades are still used in Ohio and can be found in the *Ohio Agronomy Guide* 13th Edition (Agronomy Staff 1995). Three rates of application were used for each size fraction material. They noted an increase in alfalfa yield of granulated slag at all three fineness levels that they speculated might have been a micronutrient response and reported that granulated slag was more effective than air-cooled slag at the same rate and fineness grade. Jones (1968) compared two sizes of granulated furnace slag with calcitic and dolomitic limestone at two rates of application. Jones noted that there was no important acid neutralizing or crop yield response performance difference of the fine versus coarser of the two slag materials. The slag did give plant responses comparable to the dolomitic limestone treatment. This study, like Jones (1968) and Munn (2003), would suggest that particle size distribution of the slag particles was not as good a predictor of overall acid neutralizing effectiveness as it has proven to be for carbonate forms of lime such as calcitic and dolomitic limestone.

The Mehlich III extractant was apparently dissolving a large amount of non-exchangeable Ca and Mg from the 25 g of $CaCO_3$ equivalent kg^{-1} of soil material rate of application for all three slags and for the reagent grade $CaCO_3$. The cmoles of Ca and Mg exceeded the reported CEC, and the Penn State Ag Analytical Lab soil test reports contained a warning or flag that there was apparent recovery of soluble Ca and/or Mg from the samples beyond the normally exchangeable amounts. Soil cation exchange capacity is calculated by summing exchangeable Ca, Mg, K, and acidity and a smaller

TABLE 6

Corn and soybean plant seedling tissue mineral composition at 25 g kg^{-1} rate.

Treatment	N	P	K	Ca	Mg	Mn	Fe	Zn	Al
	(%)					(mg kg^{-1})			
Corn									
Control Unlimed	9.62	0.41	2.12	0.56	0.37	390	1307	319	6519
BFS (25 g kg^{-1})	2.79	0.15	2.16	0.48	0.31	108	47	19	8.6
NMSS (25 g kg^{-1})	2.57	0.12	1.72	0.68	0.32	52	62	9	11.5
MSS (25 g kg^{-1})	2.84	0.13	1.79	0.64	0.25	48	52	11	8.4
$CaCO_3$ (25 g kg^{-1})	2.75	0.12	1.95	0.69	0.14	14	53	10	23.1
LSD (0.05)	0.23	0.01	0.14	0.05	0.01	12	10	10	13.4
Soybean									
Control Unlimed	—	0.27	1.80	0.26	0.30	148	238	133	287
BFS (25 g kg^{-1})	—	0.19	1.30	1.62	0.70	98	199	52	68
NMSS (25 g kg^{-1})	—	0.14	1.27	1.72	0.64	89	192	31	48
MSS (25 g kg^{-1})	—	0.14	1.26	1.82	0.59	87	204	36	64
$CaCO_3$ (25 g kg^{-1})	—	0.12	1.22	2.03	0.32	18	123	25	76
LSD (0.05)	—	0.13	0.25	0.24	0.07	35	111	8	156

number was used by the Penn State Lab for the exchangeable Ca for this summation than the Ca extracted by the Mehlich III reagent.

The very high levels of iron in these steel slags is not bio-available in the conditions of this study, which would be expected if it is metallic iron as the slag is introduced to the soil environment. The soil iron would go through cycles of wetting and drying that would promote oxidation of the iron in the slags to oxides or hydroxides, and indeed the iron sulfide minerals in the mine spoil also undergo further change with wetting and drying cycles resulting in the generation of additional sulfuric acid and new iron compounds, but no attempt was made to study iron speciation in this work.

Work conducted in the greenhouse during 1998, 1999, and 2000 comparing the effectiveness of contemporary steel industry slags with reagent grade $CaCO_3$ as liming material showed that these materials are useful as liming compounds. No adverse consequences were noted from the materials at the rates and conditions used. All three of the steel slags did have very low fineness efficiencies (Troeh and Thompson 1993) because of the coarse particle size of the material provided, which would need to be reduced by grinding and sieving in order to be spread uniformly and to react rapidly with soil acidity. Particle size effectiveness coefficients as used for $CaCO_3$ forms of lime may underestimate effectiveness of these slag materials because they were more effective at neutralizing acidity and promoting plant growth on acid mine soil than their fineness efficiency would suggest when it was calculated with activity coefficients used with carbonate limestones.

ACKNOWLEDGMENTS. The author would like to thank Ohio State-ATI students Jody Short, who started the first greenhouse study as a special problem, and Terri Bishop, who assisted with some of the greenhouse study care as a student research assistant. My colleagues Warren Dick, Sha Rahnema, Sam Woods, and Mike Fulton made helpful suggestions with the manuscript. Mr. Bert Bishop (OARDC Staff Statistician) is acknowledged for assistance with the statistical analyses. Appreciation is expressed to Mrs. Jill Gallion for her assistance with preparation of the manuscript. Financial assistance from the Ohio State-ATI Research and Scholarly Activity Committee and Stein, Inc., of Broadview Heights, OH, to pay for soil and plant testing and student research assistance are gratefully acknowledged.

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